Theory of metastable group-IV alloys formed from CVD precursors

Peihong Zhang,[1] Vincent H. Crespi,[1] Eric Chang,[2] Steven G. Louie,[2] and Marvin L. Cohen[2]
[1]*Department of Physics, The Pennsylvania State University, 104 Davey Lab, University Park, Pennsylvania 16802-6300*
[2]*Department of Physics, University of California at Berkeley, Berkeley, California 94720*
and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
(Received 4 February 2001; revised manuscript received 29 May 2001; published 8 November 2001)

Using chemical-vapor deposition (CVD) precursors, group-IV compounds such as Si_4C and Ge_4C, which incorporate 20 at.% carbon, have been synthesized. Here we present systematic *ab initio* studies of the electronic and structural properties of group-IV compounds formed from CVD precursors. We also propose a class of precursor molecules for materials containing 25 at.% carbon. These compounds are energetically comparable to already synthesized materials (e.g., Ge_4C) and are semimetallic within the local-density approximation. In addition, we give information for two previously proposed group-IV compounds, Si_2Sn_2C and Ge_3SnC, which are direct-gap semiconductors and match the lattice of silicon to within 1%.

DOI: 10.1103/PhysRevB.64.235201 PACS number(s): 71.20.Nr, 61.66.Fn, 61.50.Lt

I. INTRODUCTION

Group-IV alloys have attracted considerable interest recently due to their wide tunability in both structural and electronic properties.[1–15] Incorporation of substitutional carbon into other group-IV semiconductors is of particular interest. On one hand, the small radius of carbon might help reduce the lattice mismatch between band-gap-engineered Si/Ge materials and the silicon substrate; on the other hand, the presence of strongly electronegative carbon atoms, along with the strain introduced by them, offers a unique way to tailor the electronic structure with a compelling possibility of obtaining direct-gap group-IV semiconductors whose lattices match silicon.[16] With newly developed ultrahigh-vacuum chemical-vapor deposition (UHV-CVD),[10,11] group-IV compounds such as Si_4C and Ge_4C, which contain 20 at.% of carbon, have been synthesized. Here we present *ab initio* results on the electronic and structural properties of group-IV materials, namely, Si_4C, Ge_4C, Sn_4C, Si_2Sn_2C, and Ge_3SnC, which have either been synthesized or are designed to be synthesizable with UHV-CVD. In addition, we propose a different class of group-IV compounds, namely, X_6C_2 (X = Si, Ge, or Sn), which incorporate as high as 25 at.% carbon and are accessible to current synthesis techniques.

Although there has long been speculation that alloying carbon with other group-IV materials might produce interesting properties, little progress was made towards this goal until recently. The major obstacle for synthesizing group-IV compounds with high concentrations of carbon is that the solubility of carbon in silicon is very low: less than 10^{-4} at.% at the silicon melting point; in germanium the solubility is negligible. Fortunately, recent advances in synthesis have demonstrated that tetrahedral group-IV compounds containing high concentrations of carbon are possible.[1–3] More recently, Kouvetakis *et al.* reported a synthesis[10,11] based on UHV-CVD that allows the production of semiconductor alloys with well-defined (and thermodynamically inaccessible) 1:4 C:Si and C:Ge stoichiometries through the use of precursor molecules that build in the required interatomic bonding, for example, $C(SiH_3)_4$. The terminal groups (e.g., H or D) are eliminated to produce the pure C/Si (or C/Ge) ordered alloys, such as Si_4C or Ge_4C. Although Sn_4C has not been synthesized yet,[17] we extend our study to this compound for comparison purposes and to gain a better understanding of the general trends arising from differences in electronegativity and core radii.

One can build in even higher concentrations of carbon using $C_2(SiX_3)_6$ and $C_2(GeX_3)_6$ as precursors for solid Si_6C_2 or Ge_6C_2. Although these two compounds contain C-C bonds, which have long been regarded as energetically unfavorable in group-IV alloys, our detailed *ab initio* calculations here show that they are energetically comparable to the already synthesized group-IV compounds. These highly anisotropic C-C bonds should have significant effects on the electronic and structural properties.

Another subject of interest is silicon-based optically active semiconductors. Much effort has been focused on band folding, surface states, and quantum confinement. Examples include Si-Ge superlattices,[18–21] porous silicon, silicon nanocrystals,[22] and nanowires[23–26] and recent reports of implanting boron into silicon as a means of providing spatial confinement of the charge carriers.[27] Si-Ge superlattices usually have poor optical properties.[19,20] The mechanism of light emission from porous silicon is often ascribed to quantum confinement, surface states, and/or band folding,[28–30] although the physical origin is still not fully settled. We have previously suggested a more direct solution to this problem, proposing two novel group-IV compounds, Si_2Sn_2C and Ge_3SnC, which have direct energy gaps and whose lattices match silicon to within 1%.[16] Here we provide more detailed structural information for these two compounds, and charge-density distributions for Si_2Sn_2C at Γ and X to obtain a better understanding of the unusual valence-band structure of this compound.[16]

II. COMPUTATIONAL DETAILS

We use the *ab initio* pseudopotential method[31] in the local-density approximation (LDA) with norm-conserving pseudopotentials[32] in a nonlocal form suggested by Kleinman and Bylander.[33] The parametrization of the Alder–Ceperley results[34] by Perdew and Zunger[35] is used for the

exchange correlation. For germanium and tin, scalar relativistic effects[36] are taken into account. In all of the calculations, we include the nonlinear partial-core correction[37] to account for the nonlinearity of core-valence exchange-correlation energy. The energy cutoff of the plane-wave basis is set at 60 Ryd to ensure the convergence of the calculations since all of the systems include carbon atoms. The *k*-point set is generated by the Monkhorst-Pack scheme[38] with a density of $3\times3\times3$, which would be equivalent to a *k*-point density of about $6\times6\times6$ in a more familiar two-atom diamond unit cell.

Our first step was to identify candidate crystal structures for the new group-IV alloys. Although ordered microcrystalline Si_4C and Ge_4C have been successfully synthesized,[10,11] their structural properties remain largely unknown. Here we assume a minimal unit cell for structural optimizations. The minimal unit cells of all of the systems studied contain two molecular cores of the corresponding precursors and retain the diamondlike tetrahedral bonding. The integrity of the precursor molecules (and therefore the stoichiometry of the alloys) is also maintained. The atoms are initially placed into a uniform diamondlike lattice and allowed to relax in both atomic position and unit-cell size and shape. In all cases the relaxations quickly converged and did not display soft-mode behavior; this well-behaved relaxation suggests that the final relaxed structures are situated in relatively stable local minima. We then use these relaxed structures for band-structure calculations. Since the electronic structures in these compounds follow predominately from the chemical effects of relative size, electronegativity, and relative atomic-level spacing, we expect many of the overall trends observed to be reasonably generalizable across different atomic structures, so long as the constraints of precursor integrity are maintained.

III. STRUCTURAL AND ELECTRONIC PROPERTIES

A. Si_4C, Ge_4C, and Sn_4C

Figure 1 shows the precursor molecule $C(AX_3)_4$ (A =Si, Ge, or Sn) and a corresponding ordered crystalline structure. The smallest possible unit cell of these compounds contains ten atoms and has a body-centered tetragonal (bct) lattice. The relatively high symmetry of A_4C molecular cores results in a unique crystal structure if a minimal unit cell is assumed. In these systems, there are no nearest or second nearest carbon-carbon pairs; these are normally energetically unfavorable in group-IV alloys.[5] Since all of the group-IV compounds studied here are metastable, a measure of their stability is very important. We define the excess energy δE as the negative binding energy with respect to the constituent elemental materials in the diamond structure. For group-IV compounds containing Sn, comparing the energy with respect to gray tin may not be the best way to study their stability, since gray tin is not stable at room temperature. However, the energy difference between gray and white tin is small compared to the excess energy. Another quantity of interest regarding the stability of materials is the energetic barrier against structural phase transition. However, a study of the transition barriers, which are expected to be relatively large for covalent group-IV compounds, would involve extensive molecular-dynamics simulations. Since all of the structures investigated in this paper are locally stable with no indications of soft-mode behavior, we do not examine the energy barriers in detail. Table I shows the structural properties of these compounds. The excess energy δE for Si_4C is very small, 0.05 eV/atom, indicating the relative stability of this particular compound. The lattice constant of Si_4C differs from that of silicon by about 8.1%. This result is very close to a previous study.[5] The very large lattice mismatch between Si_4C and silicon implies that pseudomorphic growth of Si_4C

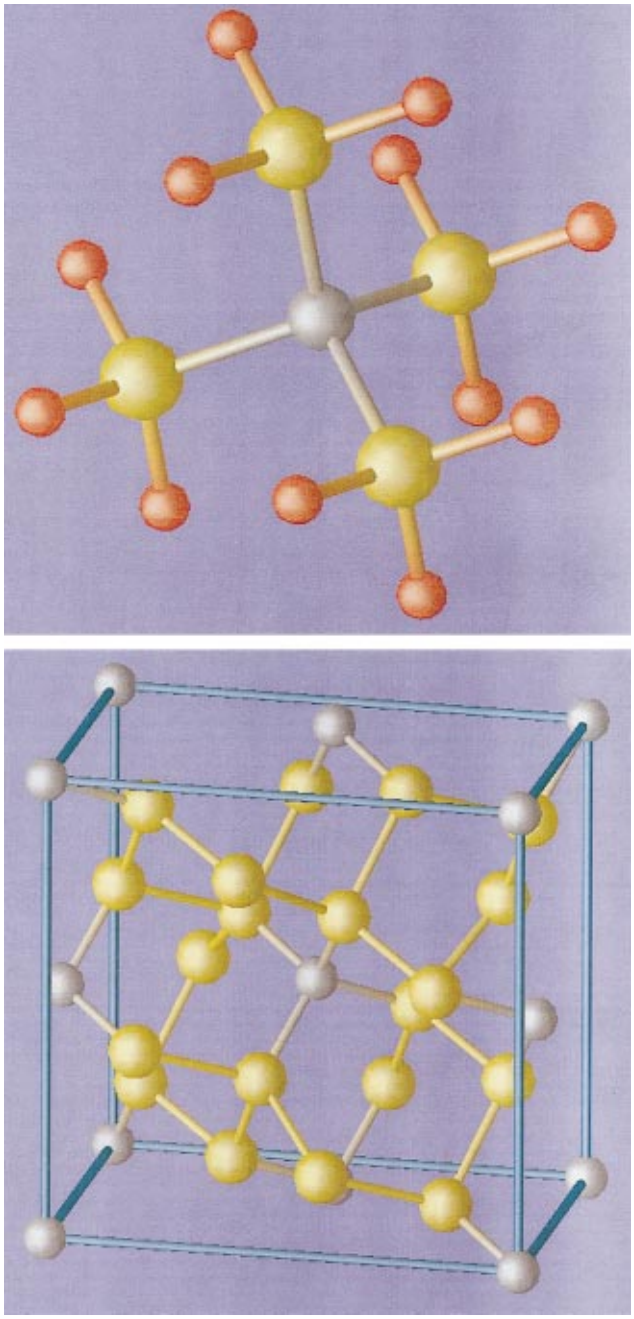

FIG. 1. (Color) Molecular precursors and a corresponding relaxed crystalline phase of Si_4C. Silicon is yellow, carbon is gray, and the terminal group is red. Ge_4C and Sn_4C have similar structures.

TABLE I. Structural properties of X_4C in the local-density approximation. The bulk moduli in parentheses are for silicon, germanium, and gray tin, respectively.

	Lattice constant (Å)	Bond length (Å)	δE (eV/atom)	Bulk modulus (GPa)
Si_4C	$a=b=7.82$	Si-Si 2.30,2.38	0.05	137
	$c=4.97$	Si-C 1.89		(100)
Ge_4C	$a=b=8.17$	Ge-Ge 2.40,2.48	0.28	108
	$c=5.22$	Ge-C 2.00		(76)
Sn_4C	$a=b=9.19$	Sn-Sn 2.77,2.86	0.42	74
	$c=5.93$	Sn-C 2.19		(47)

on silicon substrates would quickly lead to cracks or other strain-relieving defects. The lattice of Ge_4C is closer to that of silicon, with a 3.7% mismatch. Another interesting observation (which will be discussed in more detail later) is that Ge_4C becomes a direct-gap semiconductor upon lattice expansion to match silicon.

Due to symmetry breaking in these systems, there are two types of X-X (X=Si, Ge, or Sn) bonds whose bond lengths differ by about 3%, with twice as many shorter bonds as longer bonds. The weighted-average lengths of the X-X bonds are very close to those in the corresponding elemental bulk materials. For example, the Si-Si bond length as calculated by LDA is 2.332 Å, while the weighted-average Si-Si bond length in Si_4C is 2.327 Å. Si-C bonds, however, are slightly stretched compared to the bond length in binary silicon carbide (SiC), 1.89 Å vs 1.87 Å. The Ge-C bond length is 2.00 Å, which lies between those in $C(GeBr_3)_4$ (2.05 Å) and $C(GeH_3)_4$ (1.97 Å).[10] Although no stable GeC phase exists at ambient conditions, as a privilege for theorists, we can still do the calculation for this idealized compound and we find that compared to that of GeC, the Ge-C bond length in Ge_4C is stretched by 2%, similar to Si-C. The overstretched Si-C and Ge-C bonds as compared to their binary counterparts is expected in these strained systems.[10] The bulk moduli of these materials show a systematic increase from that of the dominant elemental constituent: 37% for Si_4C and 57% for Sn_4C (compared to gray tin).

Figure 2 shows the LDA band structures of Si_4C, Ge_4C, and Sn_4C. The LDA band structure of silicon, calculated on the same ten-atom unit cell, is also plotted for comparison. Although the band gaps of both Si_4C and Ge_4C are indirect, the effects of the substitutional carbon on the band structures of these systems are easily seen. First, the lowest conduction band at the Γ point is pulled down significantly. The difference between the direct energy gap at Γ and the minimum indirect gap of Si is about 2.1 eV; this difference is reduced to about 1.5 eV for Si_4C and 0.4 eV for Ge_4C. We believe this trend results from the competition between the overall volume contraction and charge transfer. Contraction in vol-

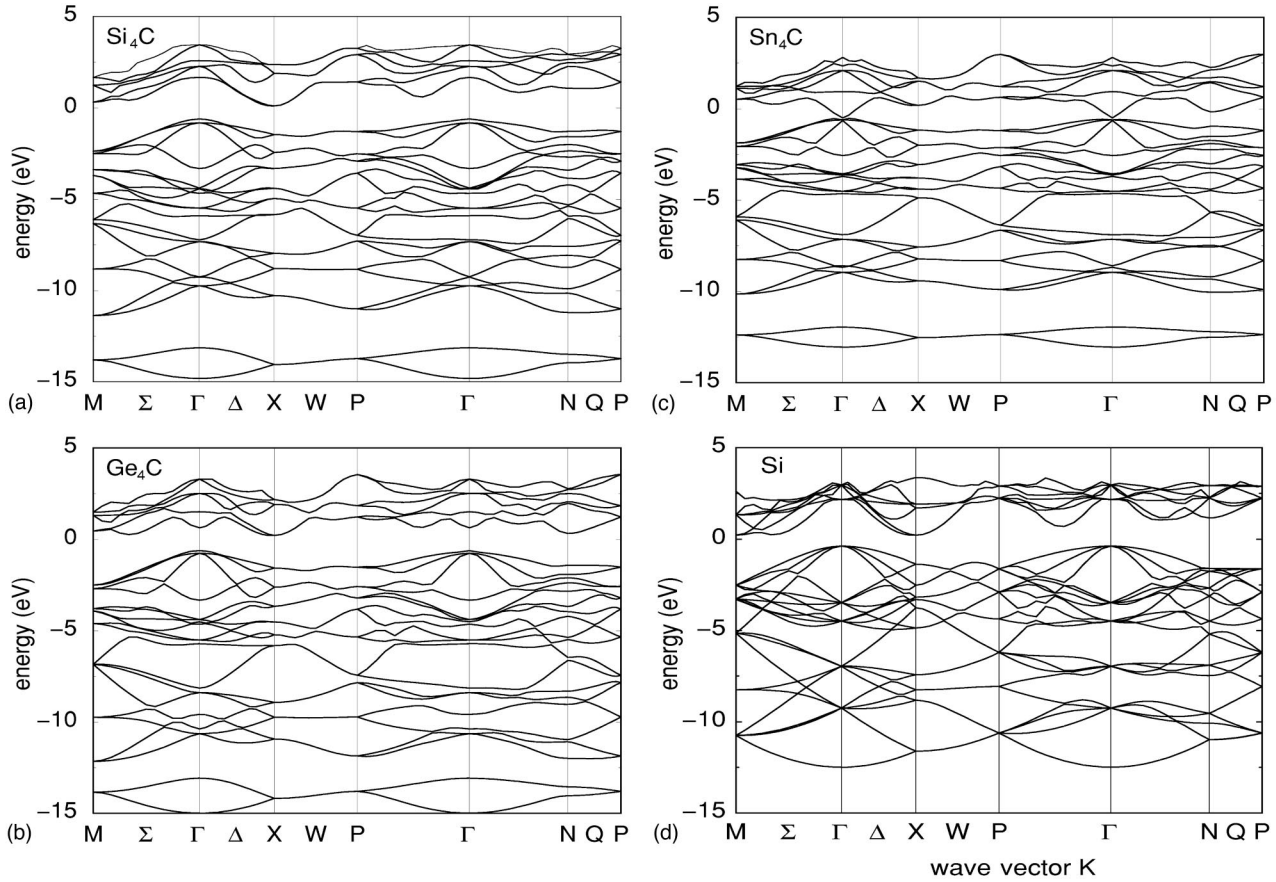

FIG. 2. Band structures of Si_4C, Ge_4C, and Sn_4C. The band structure of Si in a similar unit cell is also shown for comparison.

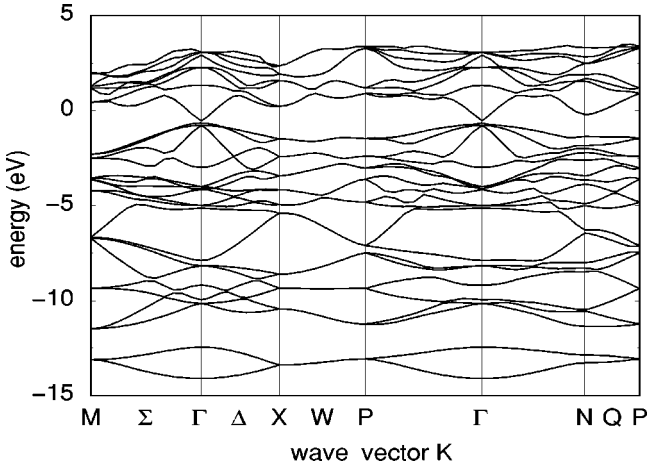

FIG. 3. Band structure of Ge_4C upon lattice expansion to match that of silicon.

ume due to the incorporation of carbon tends to lift the energy of the conduction band at Γ (relatively), while charge transfer tends to lower it. For Si_4C, charge transfer seems dominant whereas for Ge_4C, the two effects are comparable. The LDA band gap of Sn_4C is direct and slightly negative (-0.1 eV). Since LDA calculations usually underestimate the band gap of semiconductors, we expect the real band gap of Sn_4C to be moderately positive. Although Ge_4C has a indirect energy gap, upon volume expansion, it acquires a direct gap. This high sensitivity of the band gap to the lattice expansion arises from the volume variation in the local potential energy of the conduction band and is common to many group-IV materials.[39] Of the systems studied to date, only in Ge_4C does the volume effect provide a potential means to produce a direct-band-gap material on a silicon substrate, since Ge_4C is smaller than Si. In layered growth, the lattice expansion would not be isotropic, but the overall trend towards a direct gap should be maintained. Figure 3 shows the band structure of Ge_4C calculated with the silicon lattice constant, which shows the direct band gap of Ge_4C under expansion. Less than 2% lattice expansion makes the band gap of Ge_4C direct.

B. Si_2Sn_2C and Ge_3SnC

Although A_4C group-IV alloys possess interesting structural and electronic properties, they might not be good candidates for certain areas such as optoelectronic applications. Si_4C has an indirect gap and the lattice constant differs from that of silicon by as much as 8%. Ge_4C would have a direct band gap upon lattice expansion to match that of silicon. However, a 3.7% lattice expansion is too large for most practical applications. Sn_4C is expected to have a moderate direct band-gap but again does not match the lattice of silicon. Materials intermediate between Ge and Sn could have a moderate direct gap,[39] which might be achieved by incorporating tin into group-IV compounds.

Ternary group-IV compounds containing Sn, for example, CSi_ySn_{4-y} and CGe_ySn_{4-y} could be accessible to UHV-CVD synthesis techniques by replacing silicon or germanium

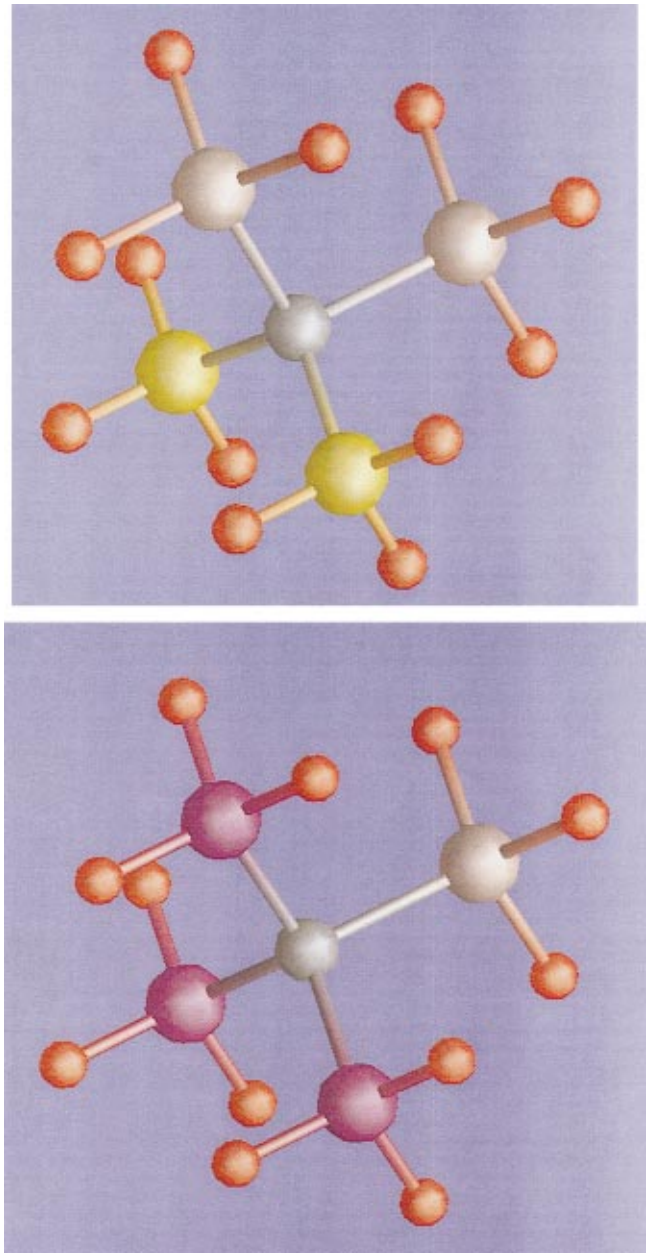

FIG. 4. (Color) Proposed molecular precursors for synthesizing Si_2Sn_2C and Ge_3SnC. C is small gray, Si is yellow, Ge is large gray, Sn is magenta, and the terminal group is red.

atoms with tin in the corresponding molecular precursors. We have shown previously[16] that silicon-compatible direct-band-gap semiconductors composed of solely group-IV elements are possible. The proposed group-IV materials are ternary alloys containing either Si, C, and Sn or Ge, C, and Sn, namely, Si_2Sn_2C and Ge_3SnC, which have direct band gaps and whose lattices match silicon to better than 1% along some low-index directions.[16] Here we provide more complete structural information and explain the unusual band-edge electronic structure of these materials. The molecular precursors proposed for synthesizing Si_2Sn_2C and Ge_3SnC are shown in Fig. 4. As to the stability of these proposed precursors, it was recently shown that molecular precursors incorporating Sn-D_3 moieties are stable for long periods (at

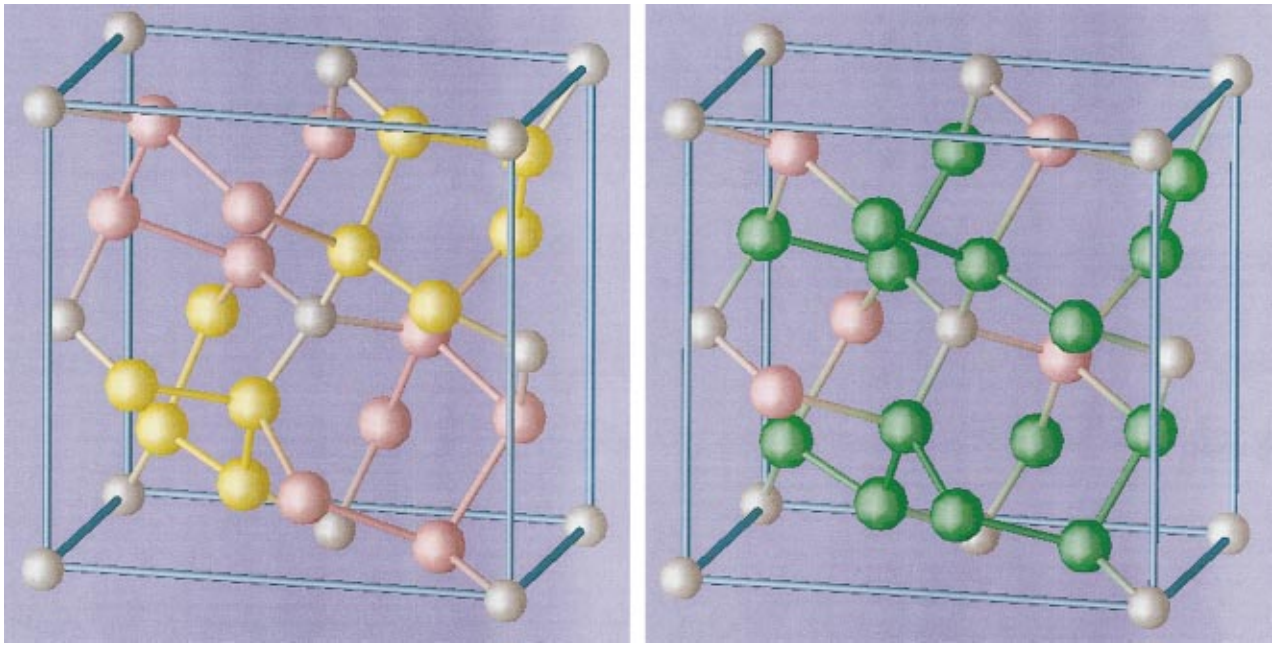

FIG. 5. (Color) Relaxed ordered structures of Si_2Sn_2C (left) and Ge_3SnC (right). C is gray, Si is yellow, Ge is green, and Sn is magenta.

0 °C).[17] (The Sn-H_3 moiety, in contrast, is known to be unstable.) Also, techniques have been developed to synthesize tetrahedral precursors where four tin atoms surround a central carbon atom.[40]

Figure 5 shows the ordered structures of Si_2Sn_2C and Ge_3SnC. Si_2Sn_2C has a bct lattice like that of the A_4C systems, but with a lower rotational symmetry. In this particular structure, there are four Sn-Sn, four Sn-Si, and four Si-Si bonds in a unit cell, thus achieving the highest possible rotational symmetry. The lattice of Ge_3SnC is slightly distorted from bct into a monoclinic structure. However, the deviation from bct is very small, about $\pm 1\%$. Therefore, we use the notation of the special (high symmetry) k points of bct structure to label the band structure of Ge_3SnC. Table II shows the structural properties of Si_2Sn_2C and Ge_3SnC. The A-C (A = Si, Ge, or Sn) bond lengths change little as compared to those in A_4C alloys, indicating the robustness and stiffness of these bonds. However, both Si-Si and Ge-Ge bonds are longer than those in Si_4C and Ge_4C due to the presence of Sn. The bulk modulus of Si_2Sn_2C is comparable to that of silicon while the bulk modulus of Ge_3SnC is similar to that of germanium. The excess energies of both Si_2Sn_2C and Ge_3SnC are moderate and comparable to that of Ge_4C, which has been successfully synthesized, indicating that these two compounds might well be accessible to current CVD techniques so long as the molecular cores of the precursors are stable under the synthesis conditions. Note that there exist lower-symmetry structures for both Si_2Sn_2C and Ge_3SnC. For Si_2Sn_2C, the lower-symmetry structure (also within a ten-atom cell) has almost the same excess energy as that of the high-symmetry one. However, the lattice of this lower-symmetry structure is distorted greatly from the ideal bct lattice. Since we focus on structures whose lattices match silicon, the badly distorted structure is less favorable and therefore will not be discussed in detail. For Ge_3SnC, the low-symmetry structure also has a more distorted lattice and furthermore shows a slightly higher excess energy (0.34 eV/atom).

TABLE II. Structural properties of Si_2Sn_2C and Ge_3SnC. All cited values are LDA results. The results for silicon calculated with a ten-atom supercell are also listed for comparison.

	Lattice constant (Å)	Bond length (Å)	δE (eV/atom)	Bulk modulus (GPa)
Si_2Sn_2C	$a=b=8.43$	Si-Si 2.36	0.30	104
	$c=5.46$	Si-Sn 2.62		
		Sn-Sn 2.72		
		Si-C 1.88		
		Sn-C 2.22		
Ge_3SnC	$a=8.50$	Ge-Ge 2.43,2.49	0.32	80
	$b=8.34$	Ge-C 2.00		
	$c=5.41$	Ge-Sn 2.58,2.66		
	$\beta=89.6°$	Sn-C 2.20		
Silicon	$a=b=8.51$	Si-Si 2.33	0.0	100
	$c=5.38$			

A very important and interesting property of these two compounds is their lattice matching to silicon along some low-index planes, for example, the (110) or (111) plane, to less than 1%. A small admixture of other molecular precursors into these two compounds might produce even better lattice matching with silicon. Another important issue regarding lattice compatability is the thermal-expansion coefficient. Although we did not study the thermal expansion compatibility between these two compounds and silicon, we would expect the difference in thermal expansion to be moderate, considering that, at room temperature, the thermal-

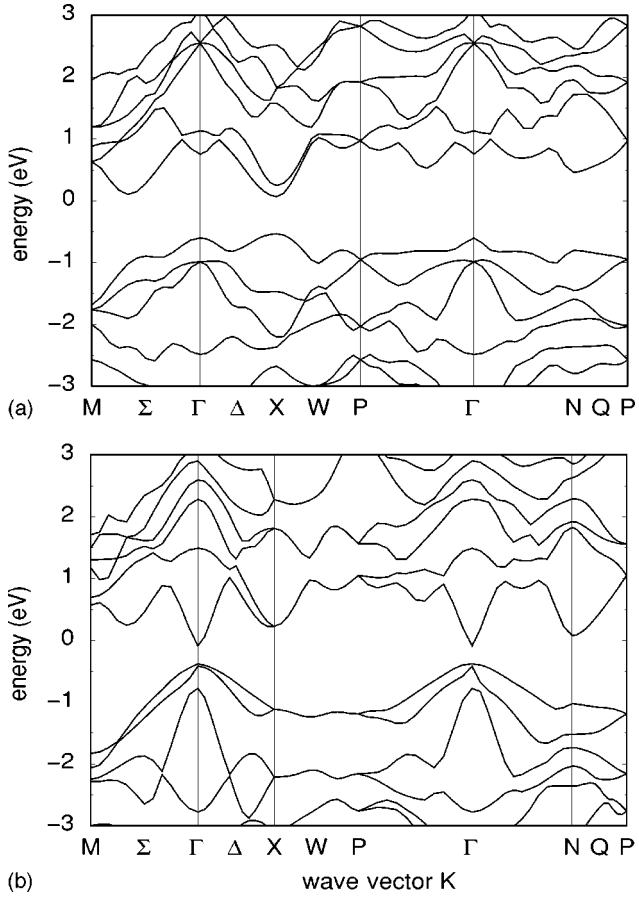

FIG. 6. LDA band structures of Si_2Sn_2C (top) and Ge_3SnC (bottom) near the band-gap.

expansion coefficient of diamond (1×10^{-6}/K) is smaller than that of silicon (about 2.5×10^{-6}/K) while both germanium (about 5×10^{-6}/K) and α-tin (about 6×10^{-6}/K) have larger thermal-expansion coefficients.

The band structures near the gap of Si_2Sn_2C and Ge_3SnC are shown in Fig. 6. Ge_3SnC has a familiar and expected direct band gap at the zone center, i.e., the Γ point. The direct band gap of Ge_3SnC can be understood as due to a large difference in electronegativity between carbon, germanium, and tin as well as the large ionic core, which tends to pull the conduction band at Γ down more rapidly than at the zone edge. Si_2Sn_2C, however, has a somewhat unusual direct band gap at the zone edge, i.e., *X* in the structure studied. Although we do see a local minimum at Γ in the lowest conduction band due to the effects similar to those in Ge_3SnC, in this case the global conduction minimum is located at *X*, which is very close to the folded *X* point in a standard two-atom diamond structure. The characteristics of the conduction band of Si_2Sn_2C, nevertheless, are not unexpected. The intriguing feature is the valence-band maximum at X, which is rarely seen in common semiconductors. To better understand this abnormal band structure, we analyze the charge density for the top of the valence band at both Γ and X. Figure 7 shows the three-dimensional charge-density isosurfaces for the top valence band at Γ and *X* for Si_2Sn_2C. The charge density at Γ concentrates around Si-Si bonds, whereas the *X*-point charge density is more localized around Sn-Sn bonds. The higher atomic levels of Sn for states associated with the valence band then account for the unusually high valence band in this part of the Brillouin zone.

C. Si_6C_2 and Ge_6C_2

In previous sections, we studied group-IV compounds isostructural with already synthesized compounds that use the propotype molecular precursor $C(AH_3)_4$, where $A=$ (Si, Ge, Sn). These systems achieve the highest carbon concentration (20 at. %) possible without creating C-C bonds or second-nearest-neighbor carbon pairs. An interesting question remains, however. Using specific molecular precursors, can group-IV compounds with higher carbon concentrations be synthesized? Such systems would inevitably contain either C-C bonds or second-nearest-neighbor carbon pairs. Although C-C bonds are thermodynamically unfavorable in group-IV alloys, if C-C bonds are built in the molecular cores of precursor molecules and are stable under film deposition, then we could expect C-C bonds to persist in the resulting alloys. We propose here two molecular precursors, $C_2(SiH_3)_6$ and $C_2(GeH_3)_6$, for synthesizing group-IV compounds with C-C bonds and 25 at. % carbon. [The $C_2(SiH_3)_6$ molecular precursor has already been synthesized by Kouvetakis.[41]] Figure 8 shows the proposed molecular precursors and sample crystalline structures, fully relaxed from LDA calculations of Si_6C_2. This structure corresponds to a particular choice of the unit cell, i.e., the smallest one. Both Si_6C_2 and Ge_6C_2 have a monoclinic lattice, which is a slight distortion from bct. For Si_6C_2, the distortion is very small, less than 0.1% while for Ge_6C_2, it is about 1.0%. To a reasonable approximation, we can still use the more familiar *k*-point notation of the bct structure for these two compounds.

Table III shows the structural properties of these two compounds. Considering that the fraction of C-C bonds is large, 1/16, the excess energy of these two compound is lower than expected. For Si_6C_2, the excess energy is 0.2 eV/atom, which is lower than that of Ge_4C. One curious result is that the C-C bond in Si_6C_2 is longer than the normal bond length in diamond: 1.55 Å vs 1.53 Å (both are LDA values), whereas for Ge_6C_2, the C-C bond is shorter than the normal one, only 1.50 Å. The strong Si-C bonds, which effectively pull the two carbon atoms apart to minimize the strain energy, might explain the slightly longer C-C bond length in Si_6C_2. For Ge_6C_2, the relatively weak Ge-C bonds, coupled with stronger C-C bonds due to charge transfer from Ge atoms to C atoms, imply that shorter C-C bonds are the optimal strain-relief configuration. Due to the lowering in symmetry, there are two types of *A*-C ($A=$Si or Ge) bonds. The weighted-average Si-C and Ge-C bond lengths are 1.93 Å and 2.05 Å, respectively, substantially longer than the normal Si-C and Ge-C bonds. The existence of C-C bonds defines a particular direction along which the bond length of both Si-Si and Ge-Ge bonds vary significantly. For example, the length of Si-Si bonds along the direction defined by the C-C dimer varies widely from 2.27 to 2.48 Å. In constrast, the Si-Si bonds more perpendicular to the C-C dimers are

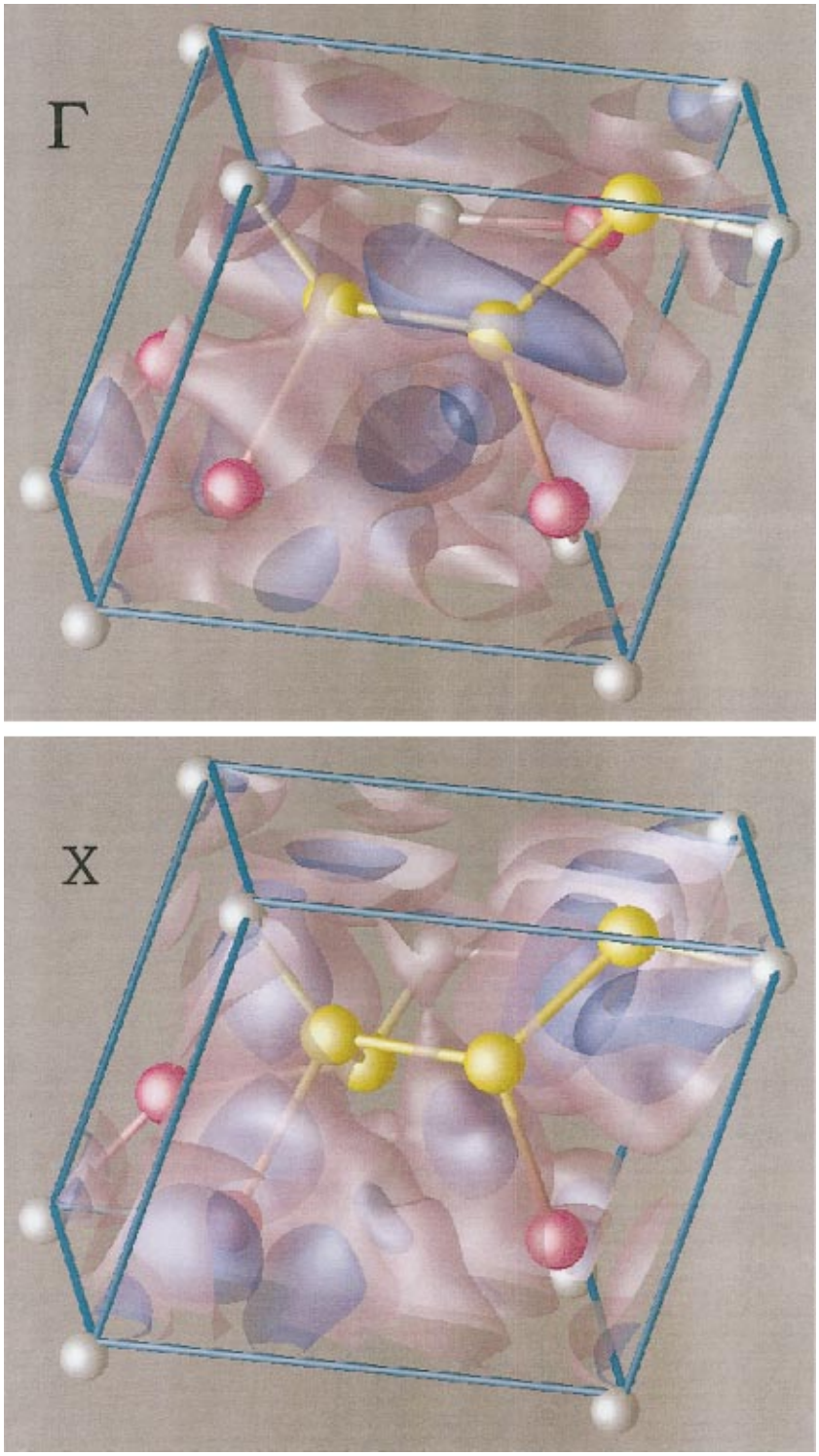

FIG. 7. (Color) Charge-density isosurfaces for the top of the valence band at Γ (top) and *X* (bottom) in Si_2Sn_2C. Electrons are localized around Si-Si bonds (in yellow) for the Γ state whereas for the X state, they are localized around Sn-Sn bonds (in magenta).

closer to the bulk value, varying from 2.29 to 2.32 Å. The overstretched Si-Si bonds along the C-C bond direction is consistent with the observation that there is substantial strain on the C-C bonds. Similar results are seen for Ge_6C_2.

Figure 9 shows the LDA band structures of Si_6C_2 and Ge_6C_2. Both alloys are metallic within the local-density approximation. This kind of strain-induced reduction of the band gap has been reported before.[4] However, we are not convinced that Si_6C_2 is indeed metallic since LDA usually underestimates the band gap and in some cases, semiconductors become metallic in LDA calculations. Since the band overlap for Si_6C_2 is small, less than 0.5 eV, Si_6C_2 might have a small direct gap if quasiparticle calculations are carried out. For Ge_6C_2, the band overlap is large and we do not necessarily expect quasiparticle corrections to fully open the gap. Notice that although the conduction and valence bands overlap at Γ, we still can see a ''quasidirect'' gap, which is evidence of increasing ionicity, i.e., charge transfer between Si

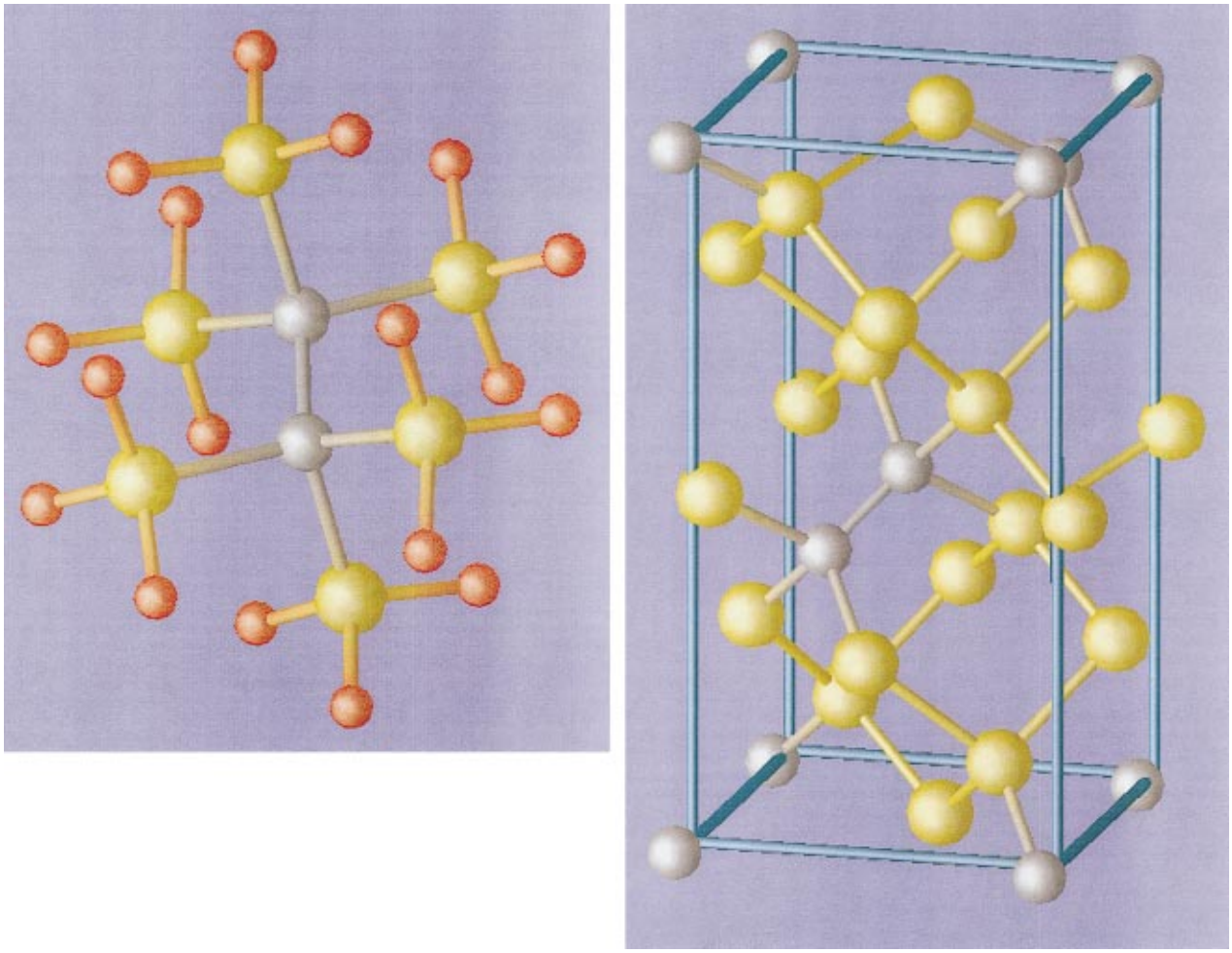

FIG. 8. (Color) Proposed molecular precursor for synthesizing Si_6C_2 and the corresponding relaxed crystalline structure. The molecular precursor and crystal structure of Ge_6C_2 are similar to those above.

(Ge) and C in these group-IV compounds. Another consequence of the large ionicity, possibly along with symmetry breaking, is that the lowest valence band is completely split off from the rest of the valence bands and is very flat, indicating that this band is very localized (on carbon). Density-of-states plots for Si_6C_2 and Ge_6C_2 are shown in Fig. 10.

TABLE III. Structural properties of Si_6C_2 and Ge_6C_2. The lattice notation of bct structure is used since both structures are only slightly distorted from bct.

	Lattice constant (Å)	Bond length (Å)	δE (eV/atom)	Bulk modulus (GPa)
Si_6C_2	$a=b\approx 4.91$	Si-Si 2.29,2.32	0.20	146
	$c\approx 9.46$	2.27,2.48		
		C-C 1.55		
		Si-C 1.90,1.99		
Ge_6C_2	$a=b\approx 5.18$	Ge-Ge 2.40,2.44	0.40	111
	$c\approx 9.84$	2.37,2.58		
		C-C 1.50		
		Ge-C 2.01,2.12		

The density of states at the Fermi level is very low, indicating an incipient gap. However it increases rapidly below or above the Fermi level. A small amount of doping might change the electronic properties of these two materials greatly. The anisotropic bonding network of both materials might produce an anisotropic phonon dispersion, while the covalent bonding and relatively strong volume sensitivity of the band structure in this class of materials could yield relatively large electron-phonon matrix elements. The large phonon frequencies of C-associated modes suggests the possibility for a moderately large superconducting transition temperature under doping heavy enough to climb out of the pseudogap.

IV. CONCLUSION

We have carried out pseudopotential density-functional-theory studies on the electronic and structural properties of group-IV alloys that either have been synthesized or are designed to be synthesizable by UHV-CVD techniques using precursor molecules that build in the desired bonding. All of the alloys studied are metastable with moderate excess energies. While the band gaps of Si_4C and Ge_4C remain indirect, the effect of substitutional carbon on the band structure is

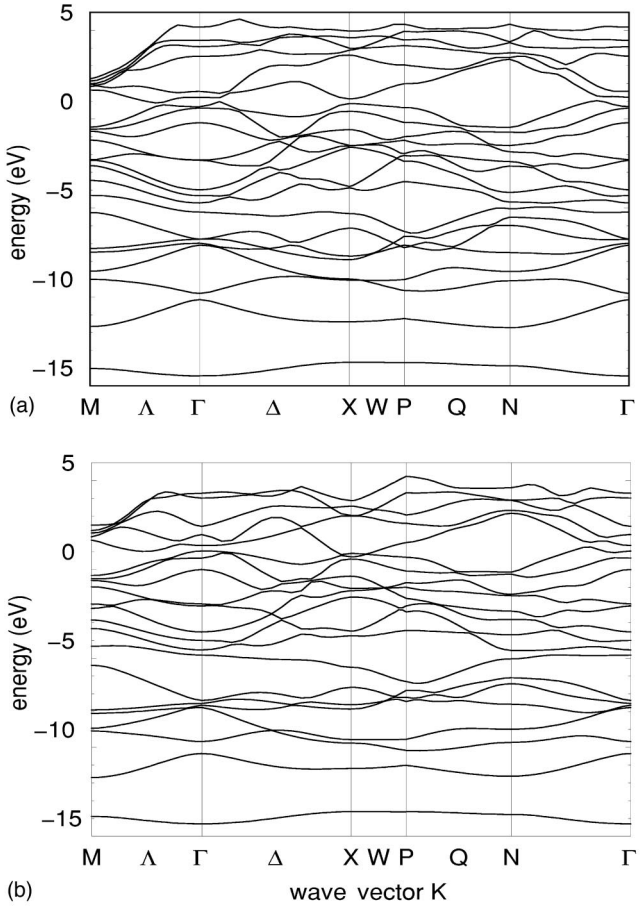

FIG. 9. LDA band structures of Si_6C_2 (top) and Ge_6C_2 (bottom).

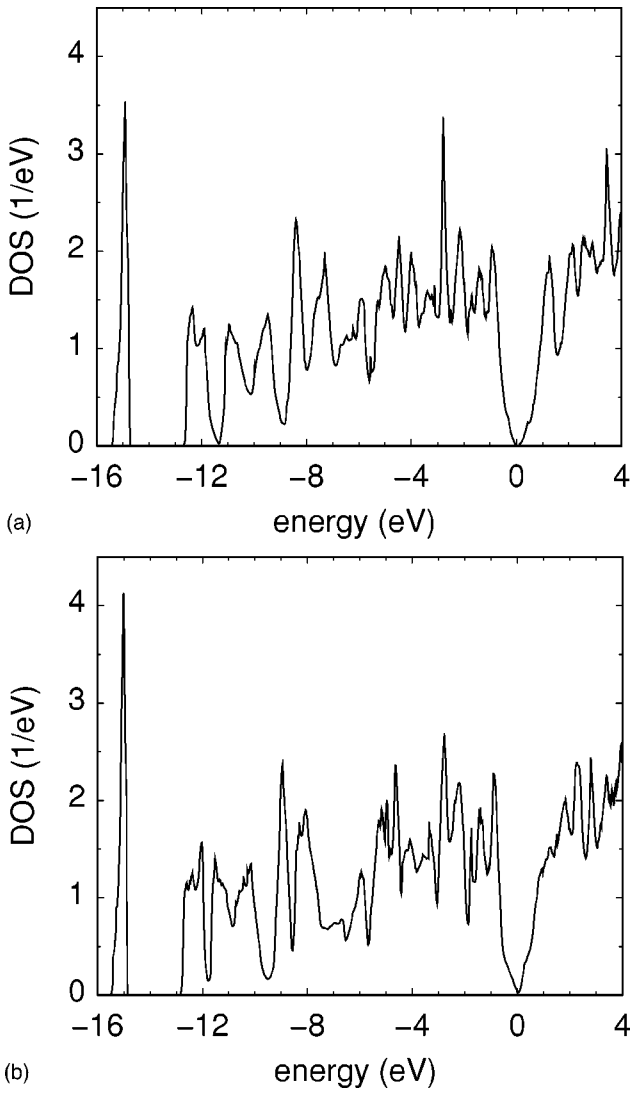

FIG. 10. Densities of states for Si_6C_2 (top) and Ge_6C_2 (bottom).

prominent. For Ge_4C, a 2% lattice expansion makes the band gap direct. Sn_4C has a direct and slightly negative LDA gap. We also presented structural information and charge-density plots for two previously proposed direct-band-gap group-IV alloys. Finally, we demonstated a new class of precursor molecules, X_2C_6 (X=Si, Ge, or Sn), which incorporates 25 at.% carbon. These high-carbon-concentration group-IV compounds exhibit interesting structural and electronic properties that might stimulate experimental search for this new class of group-IV alloys.

The idea of using CVD precursors that build in the desired chemical bonding to synthesize metastable alloys can be extended to systems beyond group-IV alloys. This technique opens great possibilities of synthesizing materials that are inaccessible to conventional thermal-equilibrium synthesis techniques. With the help of modern powerful computers and well-developed *ab initio* computational techniques, one might be able to design other specific precursors for materials with desired properties.

ACKNOWLEDGMENTS

We thank T. Mallouk and J. Kouvetakis for useful discussions. We gratefully acknowledge support from the Packard Foundation and from the National Science Foundation through Grant No. DMR-9876232. M.L.C. and S.G.L. acknowledge support from the National Science Foundation through Grant No. DMR00-87088 and from the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We also thank the National Partnership for Advanced Computational Infrastructure and the Pittsburgh Supercomputer Center for computational support.

[1] J.B. Posthill, R.A. Rudder, S.V. Hattangady, G.G. Fountain, and R.J. Markunas, Appl. Phys. Lett. **56**, 734 (1990).

[2] S.S. Iyer, K. Eberl, M.S. Goorsky, F.K. LeGoues, J.C. Tsang, and F. Cardone, Appl. Phys. Lett. **60**, 356 (1992).

[3] J.W. Strane, H.J. Stein, S.R. Lee, S.T. Picraux, J.K. Watanabe, and J.W. Mayer, J. Appl. Phys. **76**, 3656 (1994).

[4] A.A. Demkov and O.F. Sankey, Phys. Rev. B **48**, 2207 (1993).

[5] H. Rücher, M. Metthfessel, E. Bugiel, and H.J. Osten, Phys. Rev.

Lett. **72**, 3578 (1994).
[6] L. Hoffmann, J.C. Bach, and B.B. Nielsen, Phys. Rev. B **55**, 11 167 (1997).
[7] B.K. Yang, M. Krishnamurthy, and W.H. Weber, J. Appl. Phys. **82**, 3287 (1997).
[8] B.K. Yang, M. Krishnamurthy, and W.H. Weber, J. Appl. Phys. **84**, 2011 (1998).
[9] M. Ohfuti, M. Ikeda, Y. Awano, and N. Yokoyama, Phys. Rev. B **60**, 13 547 (1999).
[10] J. Kouvetakis, D. Nesting, and D.J. Smith, Chem. Mater. **10**, 2935 (1998).
[11] J. Kouvetakis, D. Chandrasekhar, and D.J. Smith, Appl. Phys. Lett. **72**, 930 (1998).
[12] G. He, M.D. Savellano, and H.A. Atwater, Appl. Phys. Lett. **65**, 1159 (1994).
[13] H. Iwano, K. Yoshikawa, A. Kojima, K. Hayashi, S. Zaima, and Y. Yasuda, Appl. Surf. Sci. **100**, 487 (1996).
[14] M.A. Berding, A. Sher, and M. van Schilfgaarde, Phys. Rev. B **56**, 3885 (1997).
[15] S. Krishnamurthy, M.A. Berding, A. Sher, M. van Schilfgaarde, and A.B. Chen, Appl. Phys. Lett. **75**, 3153 (1999).
[16] P. Zhang, V.H. Crespi, E. Chang, S.G. Louie, and M.L. Cohen, Nature (London) **409**, 69 (2001).
[17] Note that the Sn-D tetrahedra bond has recently been shown to be stable, J. Kouvetakis (private communication).
[18] T.P. Pearsall, J. Bevk, L.C. Feldman, J.M. Mannaerts, and A. Ourmazd, Phys. Rev. Lett. **58**, 729 (1987).
[19] M.S. Hybertsen and M. Schlüter, Phys. Rev. B **36**, 9683 (1987).
[20] S. Froyen, D.M. Wood, and A. Zunger, Phys. Rev. B **37**, 6893 (1988).
[21] E. Kasper, Phys. Scr. T **T35**, 232 (1991).
[22] L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzó, and F. Priolo, Nature (London) **408**, 440 (2000).
[23] L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[24] A.G. Cullis and L.T. Canham, Nature (London) **353**, 335 (1991).
[25] A.M. Morales and C.M. Lieber, Science **279**, 208 (1998)
[26] Y.F. Zhang, Y.H. Tang, N. Wang, D.P. Yu, C.S. Lee, I. Bello, and S.T. Lee, Appl. Phys. Lett. **72**, 1835 (1998).
[27] W.L. Ng, M.A. Lourenco, R.M. Gwilliam, S. Ledain, G. Shao, and K.P. Homewood, Nature (London) **410**, 192 (2001).
[28] A.J. Read, R.J. Needs, K.J. Nash, L.T. Canhan, P.D.J. Calcott, and A. Qteish, Phys. Rev. Lett. **69**, 1232 (1992).
[29] F. Buda, J. Kohanoff, and M. Parrinello, Phys. Rev. Lett. **69**, 1272 (1992).
[30] G.D. Sanders and Y.C. Chang, Phys. Rev. B **45**, 9202 (1992).
[31] J. Ihm, A. Zunger, and M.L. Cohen, J. Phys. C **12**, 4409 (1979).
[32] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1990).
[33] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[34] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[35] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[36] D.R. Hamann, Phys. Rev. B **40**, 2980 (1989).
[37] S.G. Louie, S. Froyen, and M.L. Cohen, Phys. Rev. B **26**, 1738 (1982).
[38] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).
[39] J.L. Corkill and M.L. Cohen, Phys. Rev. B **47**, 10 304 (1993).
[40] K.W. Klinkhammer, S. Kühner, B. Regelmann, and J. Weidlein, Organometall. Chem. **496**, 241 (1995).
[41] J. Kouvetakis (private communication).